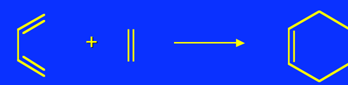
The Diels-Alder Reaction

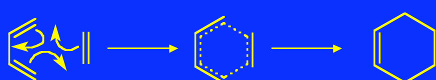
Synthetic method for preparing compounds containing a cyclohexene ring

In general...

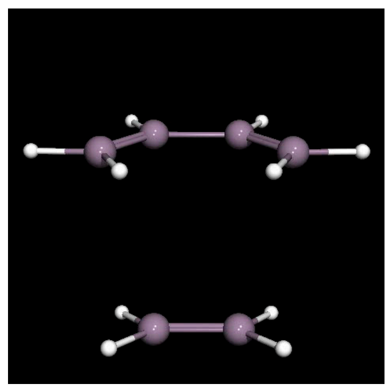


conjugated diene — alkene (dienophile) — cyclohexene

via



transition state



Mechanistic features

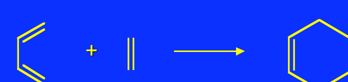
concerted mechanism

[4+2] cycloaddition

pericyclic reaction

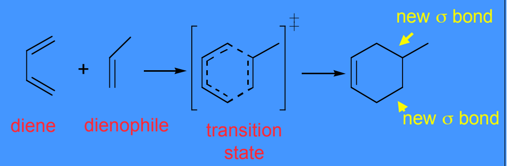
a concerted reaction that proceeds through a cyclic transition state

Recall the general reaction...



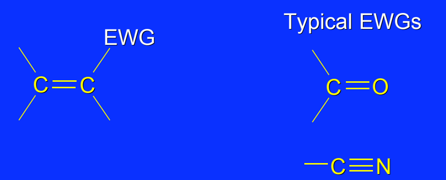
conjugated diene — alkene (dienophile) — cyclohexene

The equation as written is somewhat misleading because ethylene is a relatively unreactive dienophile.

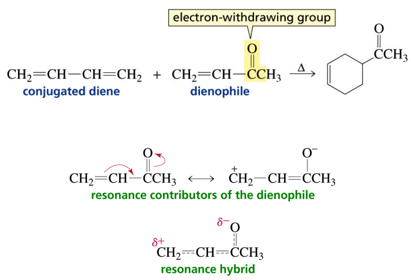


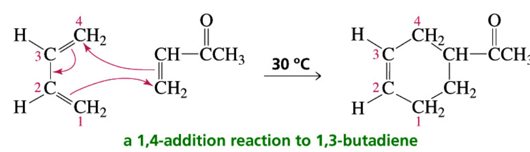
What makes a reactive dienophile?

The most reactive dienophiles have an electron-withdrawing group (EWG) directly attached to the double bond.

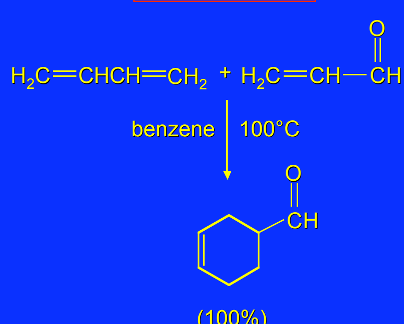


http://www.brunel.ac.uk/depts/chem/ch241s/re_view/barry/diels2.htm

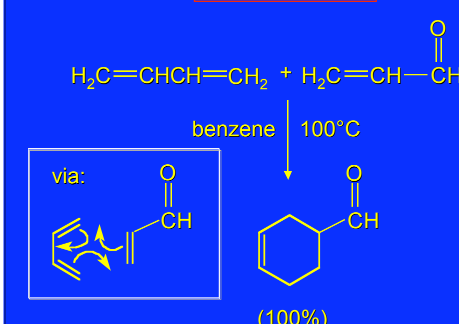




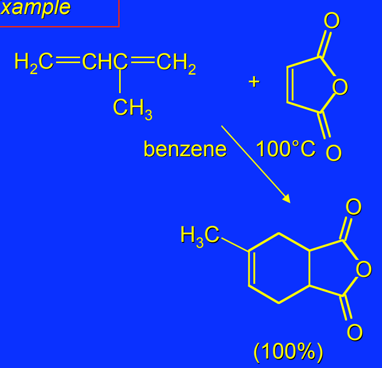
Example



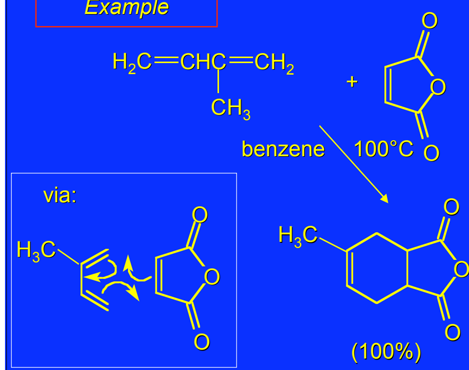
Example



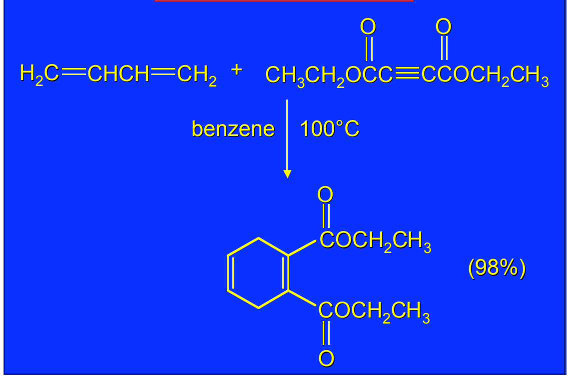
Example



Example



Acetylenic Dienophile



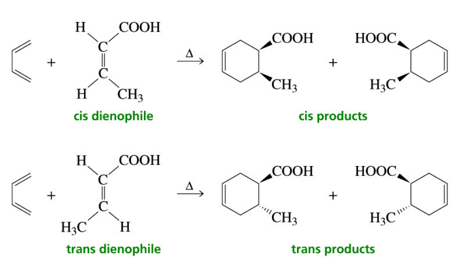
*Diels-Alder Reaction is Stereospecific**

syn addition to alkene

cis-trans relationship of substituents on alkene retained in cyclohexene product

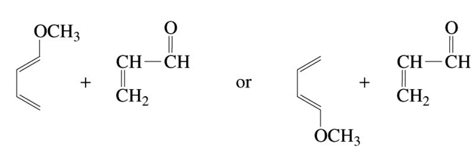
**A stereospecific reaction is one in which stereoisomeric starting materials give stereoisomeric products; characterized by terms like syn addition, anti elimination, inversion of configuration, etc.*

Stereospecific, concerted, syn addition:

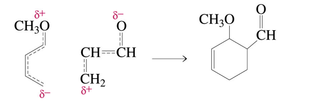


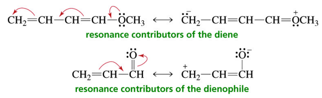
Predict the reaction products:

1. Consider the alignment of the reactants



2. Consider the charge distribution in each of the reactants

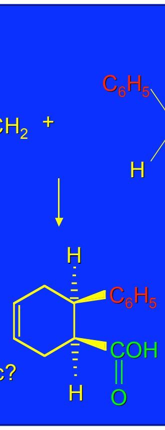




Example

$H_2C{=}CHCH{=}CH_2$ +

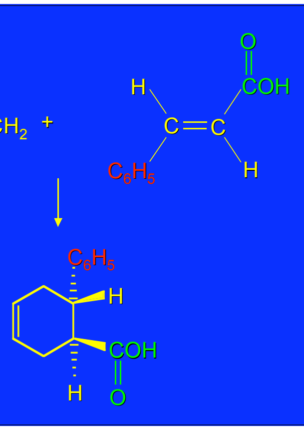
Only the s-cis conformation of the diene can participate in a Diels–Alder reaction



Only product.
But, is it enantiomeric?

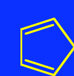
Example

$H_2C{=}CHCH{=}CH_2$ +



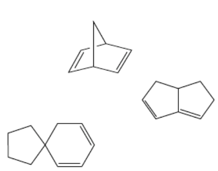
only product

Cyclic dienes yield bridged bicyclic Diels-Alder adducts.

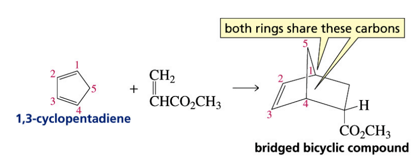


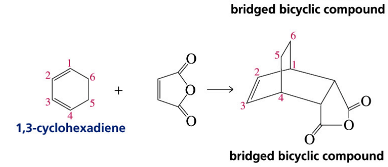
Touch a label on the left to see the corresponding atoms, groups, or molecules.

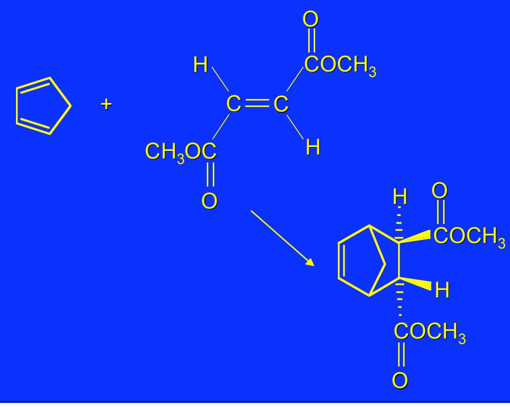
bicyclic compounds
bridged bicyclic compound
fused bicyclic compound
spirocyclic compound
isolated double bonds
conjugated double bonds
s-cis conformation
s-trans conformation

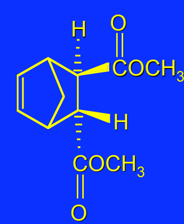


Since only cis dienes can participate in Diels–Alder reactions: 5- & 6- membered rings are ideal





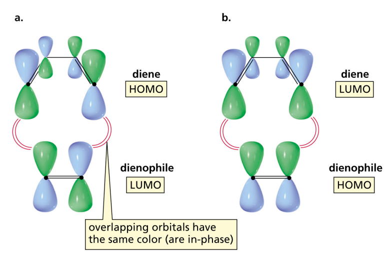




is the same as

The π Molecular Orbitals
of
Ethylene and 1,3-Butadiene

Reactants' HOMO and LUMO

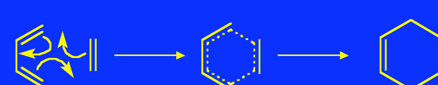


Orbitals and Chemical Reactions

A deeper understanding of chemical reactivity can be gained by focusing on the *frontier orbitals* of the reactants.

Electrons flow from the highest occupied molecular orbital (HOMO) of one reactant to the lowest unoccupied molecular orbital (LUMO) of the other.

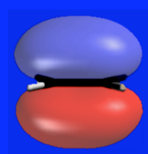
Orbitals and Chemical Reactions



We can illustrate HOMO-LUMO interactions by way of the Diels-Alder reaction between ethylene and 1,3-butadiene.

We need only consider only the π electrons of ethylene and 1,3-butadiene. We can ignore the framework of σ bonds in each molecule.

The π MOs of Ethylene

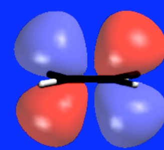


red and blue colors distinguish sign of wave function

bonding π MO is antisymmetric with respect to plane of molecule

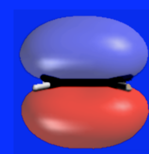
Bonding π orbital of ethylene; two electrons in this orbital

The π MOs of Ethylene



Antibonding π orbital of ethylene; no electrons in this orbital

LUMO



HOMO

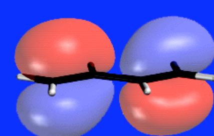
Bonding π orbital of ethylene; two electrons in this orbital

The π MOs of 1,3-Butadiene

Four *p* orbitals contribute to the π system of 1,3-butadiene; therefore, there are four π molecular orbitals.

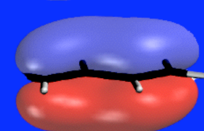
Two of these orbitals are bonding; two are antibonding.

The Two Bonding π MOs of 1,3-Butadiene



HOMO

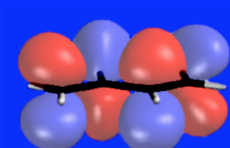
4 π electrons; 2 in each orbital

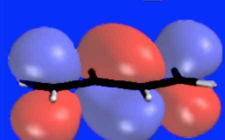


Lowest energy orbital

The Two Antibonding π MOs of 1,3-Butadiene

Highest energy orbital

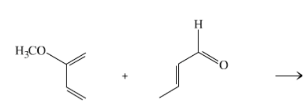




LUMO

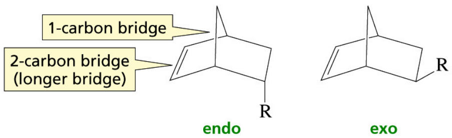
Both antibonding orbitals are vacant

Click on all of the atoms that have an unhybridized *p*-orbital, and then click "Done."

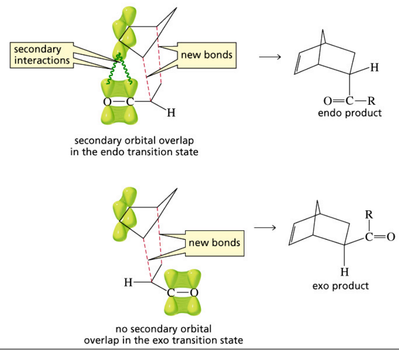


Done

Two Possible Configurations of Bridged Bicyclic Compounds

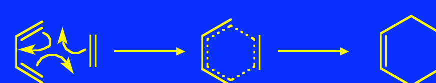


Secondary orbital overlap favors the endo product formation



A π Molecular Orbital Analysis
of the
Diels-Alder Reaction

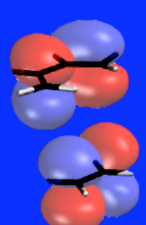
MO Analysis of Diels-Alder Reaction



Inasmuch as electron-withdrawing groups increase the reactivity of a dienophile, we assume electrons flow from the HOMO of the diene to the LUMO of the dienophile.

MO Analysis of Diels-Alder Reaction

HOMO of 1,3-butadiene



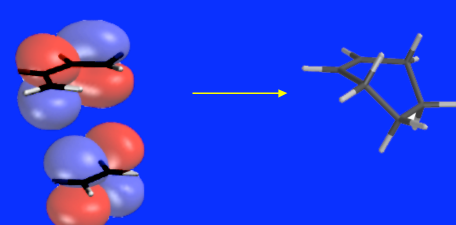
HOMO of 1,3-butadiene and LUMO of ethylene are in phase with one another

allows σ bond formation between the alkene and the diene

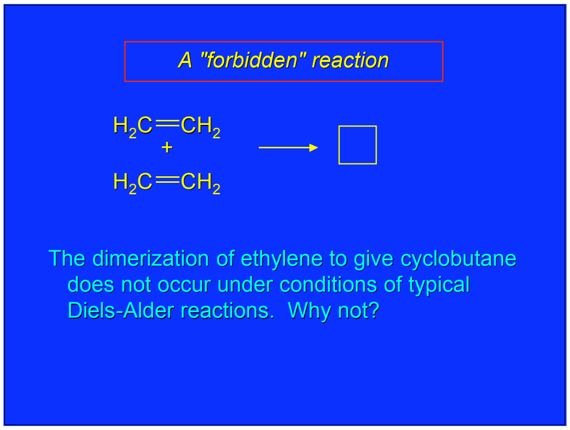
LUMO of ethylene (dienophile)

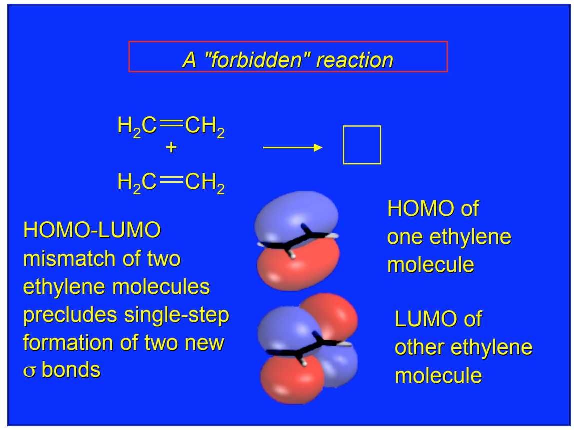
MO Analysis of Diels-Alder Reaction

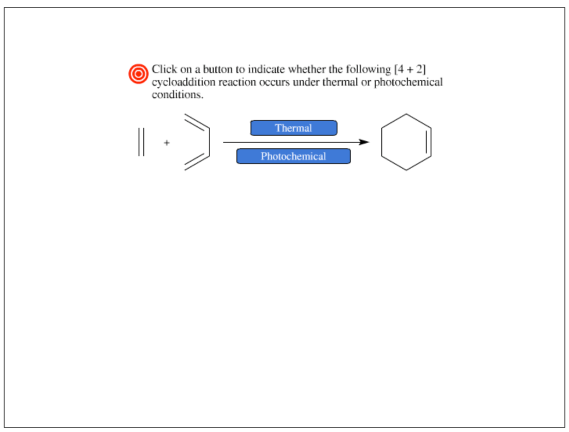
HOMO of 1,3-butadiene



LUMO of ethylene (dienophile)


A "forbidden" reaction
H2C=CH2
+
H2C=CH2
The dimerization of ethylene to give cyclobutane does not occur under conditions of typical Diels-Alder reactions. Why not?


A "forbidden" reaction
H2C=CH2
+
H2C=CH2
HOMO-LUMO mismatch of two ethylene molecules precludes single-step formation of two new σ bonds
HOMO of one ethylene molecule
LUMO of other ethylene molecule


Click on a button to indicate whether the following [4 + 2] cycloaddition reaction occurs under thermal or photochemical conditions.
+
Thermal
Photochemical